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Neutralization of Abatement Derived Sulfuric Acid

Processes Research, Inc.

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Neutralization of Abatement Derived Sulfuric Acid

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16. Abstracts The report presents a flow sheet and economics for neutralizing abatement derived H_2SO_4 with milled limestone in an aqueous slurry. The resulting gypsum is deposited in a settling pond and the supernatant is recycled to slurry fresh limestone. The process is based on a literature review. Results of pertinent laboratory experiments by American Smelting and Refining Co. are also discussed. Investment requirements for neutralization facilities are approximately $775,000, $1,530,000, and $2,875,000 (1972 dollars), respectively, for daily neutralizing capacities of 100, 350, and 1000 tons of H_2SO_4. When all of the H_2SO_4 is being neutralized, the incremental abatement costs for neutralization are approximately $53, $36, and $28 per ton of sulfur, respectively. When all of the H_2SO_4 is being sold, so none is neutralized, costs for the standby neutralizing facilities having daily H_2SO_4 capacities of 100, 350, and 1000 tons add about $5, $3, and $2 per ton of H_2SO_4, respectively, to the acid production costs. A bibliography is included.

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This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for us.

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W. D. Beers

NEUTRALIZATION OF ABATEMENT DERIVED SULFURIC ACID

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SECTION I - INTRODUCTION

In the abatement of air pollution from industrial sources such as smelters, large quantities of sulfuric acid are produced. Sulfuric acid is also produced by many of the abatement processes, such as the Monsanto Cat-Ox Process, developed for comprehensive application to air pollution sources, including power generating plants. The growing oversupply of world sulfur promises uncertainty of future markets for such acid.

From an earlier study (Appendix D, Item 34), it appears that the neutralization of abatement derived sulfuric acid with limestone may be an economically and technically feasible answer to the problem of acid disposal when acid markets are not available. Therefore, an investigation was undertaken to define more fully the potential of this approach. This investigation was to include a pertinent literature search, conceptual design, and flow sheet for the neutralization of abatement derived sulfuric acid with limestone. Investment and operating costs were to be developed for daily H_2SO_4 capacities of 100 tons, 350 tons and 1000 tons.

The conceptual design and economics discussed in this report are based on review of literature. The results of pertinent laboratory experimentation by American Smelting and Refining Company are also discussed.

SECTION II - SUMMARY

In the process discussed herein, abatement derived sulfuric acid is neutralized with milled limestone in an aqueous slurry, and the resulting gypsum is deposited in a settling pond. Supernatant from the gypsum disposal pond is used to slurry the limestone. Using annual gypsum disposal ponds each twenty feet deep, the number of filled ponds which may be left exposed, with rainfall running off to the pond being filled, varies from two filled annual ponds where annual rainfall is sixty inches, to eleven filled annual ponds where annual rainfall is fifteen inches. Beyond this, the filled ponds must be covered to prevent spilling supernatant into surroundings. Instead of annual ponds, some pond cost saving might be achieved by construction of larger ponds, depending on the number of years of acid neutralization foreseen and on the pond area limits related to the expected rainfall.

The investment requirements for neutralization facilities are approximately $775,000, $1,530,000 and $2,875,000, respectively (1972 dollars), for daily neutralization capacities of one hundred tons, 350 tons and 1000 tons of H_2SO_4. When all of the sulfuric acid is being neutralized, the incremental abatement costs (1972 dollars) for neutralization are approximately $53, $36 and $28 per ton of sulfur, for neutralization facilities having daily H_2SO_4 capacities of one hundred tons, 350 tons and 1000 tons, respectively.

For example, smelter offgas pollution abatement acid plants are considered, each producing 350 tons of H_2SO_4 daily, from offgas having different concentrations. The abatement costs for the acid production alone are approximately

$78, $33 and $25 per ton of sulfur, for smelter offgas SO_2 concentrations of two, six and twelve mole percent, respectively. Hence, the combined abatement costs for acid production and neutralization are approximately $114, $69 and $61 per ton of sulfur, respectively.

When none of the sulfuric acid is being neutralized, the incremental abatement costs for neutralization are approximately $15, $9 and $6 per ton of sulfur, for neutralization facilities having daily H_2SO_4 capacities of one hundred tons, 350 tons and 1000 tons, respectively. This would add about $5, $3 and $2 per ton of H_2SO_4 to the acid production costs, respectively.

American Smelting and Refining Company (ASARCO) presented observations from laboratory neutralization of sulfuric acid with milled limestone having various fineness of grind. A "wet process" was used in one set of experiments where the limestone was reacted with dilute sulfuric acid (one hundred grams H_2SO_4 per liter). A "dry process" was used in the other experiments, where the limestone was reacted with concentrated sulfuric acid. For one limestone, with the grind ninety-five percent through 200 mesh, in the wet process, slurry pH of 6.5 was produced in thirty minutes with only seven percent excess limestone. For the same limestone and grind, in the dry process, leachate pH 6.5 was produced in sixty minutes with only three percent excess limestone. For coarser grinds, more excess limestone or more reaction time was required to produce pH 6.5.

The extent of solubilization of calcium and magnesium was also observed in the ASARCO experiments. ASARCO expressed concern regarding the potential

hazards involved in putting out on dumps, subject to rainfall, vast quantities of waste material containing tremendous amounts of soluble Epsom salts.

An obvious drawback of the slurry process discussed in this report is the need for gypsum disposal ponds. For example, the gypsum from neutralization of 350 tons of H_2SO_4 daily would annually cover seven acres with a deposit about twenty feet deep.

This leads to consideration of alternative neutralization processes accommodating the evolution of reaction heat and CO_2 to produce dry gypsum or perhaps the more useful less hydrated calcium sulfate. Suggestions regarding process alternatives are included in the recommendations. Bases for conceptual design of such alternative processes do not appear in the literature reviewed, but the dry process experiments by ASARCO are pertinent.

Deposits of the relatively firm cake produced by the ASARCO dry process would be more easily protected from rainfall than filled settling ponds. In view of the neutralization of concentrated sulfuric acid in one hour using little excess limestone, this process alternative appears quite promising.

SECTION III - RECOMMENDATIONS

A. APPLICATION OF LIMESTONE NEUTRALIZATION

Because of the associated environmental problems presented by limestone quarrying, transportation, and grinding, and by the gypsum disposal ponds, it is recommended that the process discussed in this report be considered for short range application to limited situations. This process appears ideal for the remotely located smelter which already has an abatement acid plant, provided there is a ready source of limestone. The remote location increases the difficulty of selling the acid during unfavorable market periods. On the other hand, the remote location minimizes the environmental impact of the limestone operations and the gypsum disposal ponds. Many of the remotely located smelters are in arid regions where covering filled ponds would be unnecessary.

The applicability of limestone neutralization of sulfuric acid would be significantly broadened by development of alternative processes producing firm waste instead of fluid gypsum sludge.

B. PROCESS DEVELOPMENT

It is recommended that the following experimental work be done to confirm the workability of the slurry process and to improve the basis for final design of specific facilities. This work should simulate use of limestone having high contents of magnesium and chlorides, expected to produce the most troublesome conditions.

1. Confirm the thermal balance and determine the reaction rate by laboratory experimentation, including measurement of CO_2 evolution.

2. Using pilot plant equipment, as proposed by ASARCO, determine the excess, if any, of limestone required, and determine the minimum grinding of the limestone influencing the selection of materials of construction for the slurry line to the gypsum settling pond.

3. Determine by actual trial the limitations on reaction conditions precipitating gypsum which will settle suitably in the disposal pond.

4. In connection with the gypsum precipitation work, determine the gypsum disposal pond volumetric requirements.

5. Determine whether significant amounts of SO_3 are evolved with the CO_2 under the reaction conditions producing a suitable gypsum precipitate.

C. PROCESS ALTERNATIVES

It is recommended that the following process alternatives be considered to gain the advantages of producing firm waste instead of fluid gypsum sludge. Some of the experimental work on other pollution abatement processes may have a bearing on these alternatives.

1. Filter or Centrifuge with Slurry Process

Depending on the nature of the gypsum precipitate found in the development of the slurry process, it may prove feasible to employ filters or centrifuges in the slurry process to produce a firm gypsum cake facilitating disposal. If necessary, the slurry might be held in a cooling pond before

being filtered or centrifuged. It seems noteworthy that the Chiyoda Thoroughbred 101 Flue Gas Desulfurization Process uses centrifuges to recover gypsum from slurries.

2. Paste Process

Extending the technique of the ASARCO dry process experiments, feed concentrated sulfuric acid and milled limestone into a continuous kneader mixer, with enough water to produce the desired temperature by evaporation of the excess water. The mixer discharges the paste into a rotating drum providing adequate residence time and discharging a firm gypsum waste. The CO_2, water, air and any SO_3 evolved are vented from the mixer and drum to an agitated tank of limestone slurry or lime slurry. Slurry is drawn from this tank to provide the required water in the kneader mixer.

This process would be similar in some respects to the process for producing hydrofluoric acid, in which milled fluorspar is mixed with sulfuric acid and the resulting paste heated in a rotary kiln to evaporate the HF, leaving dry gypsum byproduct.

3. Sulfur Trioxide Limestone Process

Convert the sulfur content of the acid plant feed gas to SO_3 and, instead of absorbing the SO_3 in water, pass the resulting gas through fluidized beds of milled limestone arranged for countercurrent flow, the excess water and CO_2 evolved joining the spent gas, and the dry gypsum being discharged from the last bed.

4. Sulfur Trioxide Quicklime Process

Convert the sulfur content of the acid plant feed gas to SO_3 and instead of absorbing the SO_3 in water, pass the resulting gas through fluidizing beds of quicklime, arranged for countercurrent flow, the excess water joining the spent gas and the anhydrite being discharged from the last bed.

In experiments to determine the feasibility of this process, observation should be made of the extent to which the SO_3 is decomposed to SO_2 on particle surfaces overheated by the highly exothermic reaction. Study of this process might well be started following the procedures used in studying the reaction of SO_2 and CaO, as described in December 1971, Environmental Science & Technology pages 1191-1195 "Reactions of Gaseous Pollutants with Solids I. Infra Red Study of the Sorption of SO_2 on CaO" by M. J. D. Low, Arthur J. Goodsel and Nobotsune Takezawa (Apendix D, Item 35).

SECTION IV - DISCUSSION

A. PROPOSED NEUTRALIZATION PROCESS

In the process discussed in this report, abatement derived sulfuric acid is neutralized with milled limestone in an aqueous slurry, and the resulting gypsum is deposited in a settling pond. Supernatant from the gypsum disposal pond is used to slurry the limestone. The principal reactions include the following:

$$H_2SO_4 + CaCO_3 + H_2O \longrightarrow CaSO_4 \cdot 2H_2O + CO_2 + 26{,}500 \text{ calories per gram formula.}$$

$$H_2SO_4 + MgCO_3 \longrightarrow MgSO_4 + H_2O + CO_2 + 27{,}900 \text{ calories per gram formula.}$$

The conceptual design of this process is shown in the flow diagram presented in Appendix A. Milled limestone is slurried with supernatant overflowing from the gypsum settling pond. The limestone slurry is pumped to the neutralization tank, where the sulfuric acid is added. The CO_2 evolved is vented from the neutralizer through the limestone slurry tank, to catch SO_3 vapors which may be carried by the CO_2.

The neutral slurry is pumped from the neutralizer to the gypsum settling pond. The reaction heat is dissipated by evaporation of water from the pond. The cold supernatant overflowing from the pond is diluted with water except as rainfall makes up for evaporation and for the water left in the gypsum sludge deposited in the pond.

The high magnesium content of the limestone in the example shown with the flow diagram in Appendix A results in saturation of the supernatant with

magnesium sulfate. The effects of this are mentioned later in this discussion.

B. PARALLEL PROCESS TECHNOLOGY

As no significant use has been made of this process in the past, it is necessary to base the conceptual design for neutralization of sulfuric acid with limestone on the technology of analogous chemistry commercially practiced. Two processes present promising parallels. One of these is the reaction of sulfuric acid with fluorspar to produce hydrofluoric acid and gypsum. The other is the reaction of sulfuric acid and calcium phosphate to produce phosphoric acid and gypsum.

1. Hydrofluoric Acid (HF) Technology

The HF technology is attractive because the byproduct gypsum is dry. A major point of similarity to sulfuric acid/limestone neutralization is found in the volatility of the HF and CO_2. On the other hand, a significant difference is found in the heat balance.

In the HF process, after the sulfuric acid and milled fluorspar are kneaded together, it is necessary to heat the mixture to vaporize the HF, leaving the dry gypsum residue.

The reaction of sulfuric acid with limestone is highly exothermic, producing far more heat than that required to vaporize the CO_2. The mixture of large quantities of concentrated sulfuric acid and limestone without cooling might produce local high temperatures, thus vaporizing SO_3. Therefore, the equipment requirements for mixing sulfuric acid and limestone may be quite

different from those for mixing sulfuric acid and fluorspar. Hence it appears that the HF technology is not, at present, a useful basis for the conceptual design for sulfuric acid limestone neutralization.

Nevertheless, it may be worthwhile to continue the experimental work, pertaining to this process, begun by American Smelting and Refining Company (ASARCO) to gain the advantages of producing firm waste from neutralization of sulfuric acid and limestone. This is among the process alternatives recommended for further study. The ASARCO data are reviewed in another part of this discussion.

2. Wet Phosphoric Acid Technology

The conceptual design for the slurry process discussed in this report is based largely on the parallels found in wet phosphoric acid technology. In the typical wet phosphoric acid process, sulfuric acid and calcium phosphate react to form phosphoric acid and gypsum. The gypsum is filtered from the phosphoric acid solution. The gypsum is washed with water on the filter to increase recovery of acid. The wash filtrate is used as makeup in the reaction. A principal requirement is to provide conditions producing gypsum suitable for filtering and washing.

The reaction is exothermic, and heat removal is required. Water cooling coils are quickly fouled by gypsum scaling. Heat is removed by evaporation of water, which offsets the dilution of the acid by the gypsum filter wash water. The cooling may be by flash evaporation under vacuum. The vacuum flash evaporators are operated for months between shutdowns to wash

out the gypsum scale. The reaction mixture may be cooled and the water may be evaporated by injecting air into the reacting mixture. This is troublesome, despite special devices used to minimize plugging and corrosion. The use of air also increases the fume scrubbing requirements.

Troublesome foaming is caused by CO_2 evolution from carbonate impurities in the calcium phosphate rock.

Chloride and fluoride impurities increase the severe corrosion problems inherent in the wet phosphoric acid process.

Byproduct use of the wet gypsum is seldom economical in the United States. The usual practice is to reslurry the filter cake with supernatant from a pond and to pump the slurry to a gypsum disposal pond. Dumping the wet gypsum cake has rarely been advantageous.

3. Favorable Differences

Several of the differences from the wet phosphoric acid process result in easier conditions for the sulfuric acid limestone neutralization process, as follows.

As no salable product is being recovered from the limestone, it is not necessary to filter, wash, and reslurry the gypsum. Instead, the reaction mixture may be pumped directly to the settling pond with minimal concern for completion of the reaction and gypsum crystal growth. On the other hand, while the slurry pipe to the settling pond may be carbon steel for the phosphoric acid plant, more corrosion resistance may be required for the pipe carrying imcompletely reacted sulfuric acid and limestone slurry.

Furthermore, although the gypsum precipitated in the limestone neutralization is not to be filtered, it must settle suitably in the disposal pond. This might prove to be equally as stringent a requirement as suitability for filtering.

Although the CO_2 evolution from the limestone presents a potentially greater foaming problem than the carbonate impurities in calcium phosphate rock, this need not be faced in a vacuum flash evaporative cooler. Whereas the phosphoric acid reaction is cooled by recirculating the reaction slurry through the flash evaporator, the limestone neutralization may be cooled by dilution with supernatant from the gypsum settling pond.

The corrosion conditions are expected to be much less severe with the nearly neutral brine than with the phosphoric acid reaction mixture.

C. LIMESTONE COMPOSITION

The magnesium content of the limestone is expected to be a significant variable in the slurry process discussed in this report. The effects of the magnesium content result principally from the great solubility of magnesium sulfate.

The material balance shown with the flow diagram presented in Appendix A is based on a magnesium to calcium weight ratio of about 28 to 72 in the milled limestone. This ratio was chosen to give an example in which the supernatant would be saturated with magnesium sulfate. A higher magnesium content in the limestone would result in depositing Epsom salts with the gypsum in pond sludge. A lower magnesium content in the limestone would, of course, result in a lower

magnesium sulfate concentration in the supernatant.

The magnesium contents of limestones vary widely. The two limestones used in the ASARCO experiments contained 0.5 percent and 2.0 percent magnesium by weight, in contrast to the ten weight percent magnesium content of the limestone in the flow diagram presented in Appendix A. As low magnesium limestone is required for cement manufacture, it might prove advantageous to use high magnesium limestone for neutralization of abatement derived sulfuric acid. Furthermore, valuable byproducts might eventually be derived from the rather pure magnesium sulfate solution produced.

The magnesium sulfate concentration in the supernatant, and hence in the limestone slurry, is expected to affect the reaction with sulfuric acid. The effects may include neutralization rate, CO_2 evolution, SO_3 evolution, foaming, and gypsum crystallization. These effects should be observed in the experimental work recommended in this report.

Other effects of the magnesium sulfate concentration in the supernatant include specific gravity, viscosity, specific heat, and water vapor pressure, all of which affect pump performance, operating temperatures, and evaporation from the pond.

Although limestones rarely contain significant amounts of chlorides, the chloride content of the limestone should be observed because of the adverse corrosion effects which chlorides would have on stainless steels used in the sulfuric acid neutralization system.

D. SLUDGE POND MANAGEMENT

For the typical limestone slurry neutralization facility, it appears advisable to build one sludge pond each year, each pond having capacity for one year. Pond costs are thus postponed until the need is clear. It is expected that a time may be found each year when pond construction costs will be minimum. Depending on what part of the acid is neutralized, it might even prove satisfactory to skip a year of pond building. This method of sludge pond management is reflected in the process economics presented later in this discussion.

Another benefit of ponds of annual size is accommodation of rainfall. The annual water requirements for the sludge and the annual evaporation from the pond are equivalent to about 200 inches of rainfall on one annual pond. If filled ponds were left exposed to rainfall with the runoff collected in the pond currently in use, the process would require annually the equivalent of one hundred inches of rainfall on two annual ponds, fifty inches on four ponds, twenty inches on ten annual ponds, and so on. Depending on the annual rainfall at the limestone slurry neutralization facility, this would limit the number of annual ponds which could be left exposed. Additional annual ponds would have to be covered so rain falling on them could be diverted from the other ponds without environmental pollution. Four annual ponds could be left uncovered in all but the wettest regions of the United States, such as the Gulf Coast.

Instead of annual ponds, some pond cost saving might be achieved by construction of larger ponds depending on the number of years of acid neutralization

foreseen, and on the pond area limits related to the expected rainfall.

The water balance and pond requirements are obviously affected by variation in sludge compaction. The ease of covering filled ponds and the feasibility of building dikes of dredged sludge depends on the stiffness of the sludge. In the example shown in Appendix A, there are seven pounds of gypsum and limestone per gallon of sludge, that is, 52 pounds per cubic foot, about three quarters of the density of loose, powdered gypsum. While this is a reasonable assumption, the composition and volume of the sludge remain key factors to be determined in the experimental work recommended in this report.

The water balance is also affected by the concentration of the sulfuric acid. In the example shown in Appendix A, the H_2SO_4 concentration is 93 weight percent. Not only is more water introduced with acid of lower concentration, but also there is less heat of reaction, so less water is evaporated from the pond.

E. PROCESS ECONOMICS

The economics of the limestone slurry neutralization process, expressed in 1972 dollars, are summarized in Appendix B, pages 25, 26 and 27, for daily H_2SO_4 capacities of one hundred tons, 350 tons and 1000 tons.

The costs for limestone grinding facilities are based on information presented in Sulfur Oxide Removal From Power Plant-Stack Gas: Conceptual Design and Cost Study, Sorption By Limestone or Lime: Dry Process by Tennessee Valley Authority, 1968 (Appendix D, Item 23).

In addition to the grinding facilities, the grinding and neutralization costs include the equipment indicated on the flow diagram in Appendix A, but

of proportionately lesser size for daily capacities less than 1000 tons H_2SO_4.

While land for ten annual ponds is included in the investment costs, only the first annual gypsum disposal pond is included. In the operating costs, therefore, the pond is depreciated entirely in the year when all acid is neutralized but at ten percent annually when no acid is neutralized. No additional allowance is included for covering ponds from rainfall. It might prove feasible to cover filled ponds with soil from construction of new ponds.

The costs estimated for the ponds are based on the following construction, typical of the requirements in many situations to minimize leakage of sulfate solutions to groundwater. The dikes forming the ponds are constructed of soil excavated from the interior area to a level just above the groundwater table. The bottoms of the ponds and inside slopes of the dikes are covered with a six inch thick layer composed of selected excavated material into which bentonite has been mixed. Another four inch to six inch layer of excavated material is placed on top of the bentonite-treated layer. The outside faces and tops of the dikes are finished with a layer of topsoil. The supernatant collection structure is constructed opposite the slurry inlet, and includes an adjustable weir gate and a sump for the supernatant pump. Costs of ponds may be considerably different for ponds of different construction permitted and/or required by topography, soil conditions, climate, and other site factors.

Instead of annual ponds, some pond cost saving might be achieved by construction of larger ponds, depending on the number of years of acid neutralization foreseen, and on the pond area limits related to the expected

rainfall. The initial cost for such a pond would not have the one year write-off appropriate for an annual pond, but would have a longer amortization. For a pond constructed over a number of years, with dikes built of gypsum periodically dredged from the bottom, the dredging costs would be added to the amortization of the initial cost.

Acid storage facilities are expected to be adequate in the acid plant, so none are included in the neutralization facilities, nor is standby spare equipment included. With adequate acid storage available, a brief interruption in the neutralization operation would not significantly affect the operation of the pollution abatement acid plant, or its source. Two neutralization tanks are the only dual equipment for the 1000 tons H_2SO_4 daily capacity. For facilities of greater capacity, dual ball mills might be required for limestone grinding.

The operating costs for the neutralization facilities are presented per ton H_2SO_4 for consideration with acid prices and per ton sulfur for consideration with sulfur emission abatement costs. There being no operating plant using the subject process, the operating costs are based on estimated performance, not actual experience. The allowance for maintenance, annually five percent of investment, is typical for facilities operating similar equipment. The limestone grinding facilities are expected to require more than half of the operating labor attention, the balance being required for attendance of the neutralization and pond operations. About three quarters of the power requirement is for the limestone grinding mill motor. The delivered cost of limestone,

$3 per ton, is based on information presented in the 1968 TVA study (Appendix D, Item 23), with escalation to 1972 dollars.

No cost has been assigned to water required during initial operation and at other times when there is not enough supernatant available from the pond. Some circumstances might require consideration of this cost, especially the dry seasons in arid regions.

Limestone slurry neutralization costs are presented in Appendix B, page 28, with acid plant operating costs for daily H_2SO_4 capacity of 350 tons based (for example) on abatement of smelter offgas sulfur. Acid plant operating costs are shown for SO_2 concentrations of two, six, and twelve mole percent in the smelter offgas.

The acid plant operating costs are based on information presented in Systems Study For Control of Emissions, Primary Non Ferrous Smelting Industry by Arthur G. McKee & Company, June 1969 (Appendix D, Item 29). These costs reflect the need for preheating the two mole percent SO_2 smelter offgas for conversion to SO_3.

F. AMERICAN SMELTING AND REFINING COMPANY DATA

American Smelting and Refining Company presented observations from laboratory neutralization of sulfuric acid with milled limestone having various fineness of grind. In one set of experiments a "wet process" was used, in another a "dry process" was used. Of the two, the wet process is more similar to the process discussed in this report.

The ASARCO data are shown in Appendix C. The figures have been redrawn to include the supplementary information from ASARCO.

In the wet process experiments, dilute sulfuric acid (one hundred grams H_2SO_4 per liter) was reacted with limestone for a period of time, and the slurry pH was observed. For one limestone, about 107 percent of the stoichiometric ratio of limestone to acid produced slurry pH 6.5 in thirty minutes with the grind ninety-five percent through 200 mesh, and in 6.5 hours with the grind thirty-nine percent through 200 mesh. For this limestone, with the grind thirty-nine percent through 200 mesh, about 151 percent of the stoichiometric ratio of limestone to acid produced slurry pH 6.5 in thirty minutes. For the other limestone, with the grind sixty-one percent through 200 mesh, about 144 percent of the stoichiometric ratio of limestone to acid produced slurry pH 6.5 in thirty minutes.

In the dry process experiments, concentrated sulfuric acid was reacted with limestone for one hour, the cake was then leached with water, and the pH of the resulting solution was observed. For one limestone, with the grinds ninety-five percent and thirty-nine percent through 200 mesh, about 103 percent and 197 percent, respectively, of the stoichiometric ratio of limestone to acid produced pH 6.5. For the other limestone, with the grinds ninety-one percent and sixty-one percent through 200 mesh, about 122 percent and 160 percent, respectively, of the stoichiometric ratio of limestone to acid produced pH 6.5.

The extent of solubilization of calcium and magnesium was also observed in these experiments. Although the two limestones contained only 0.5 percent and 2.0 percent magnesium, ASARCO expressed concern regarding the potential hazards involved in putting out on dumps, subject to rainfall, vast quantities of waste material containing tremendous amounts of soluble Epsom salts.

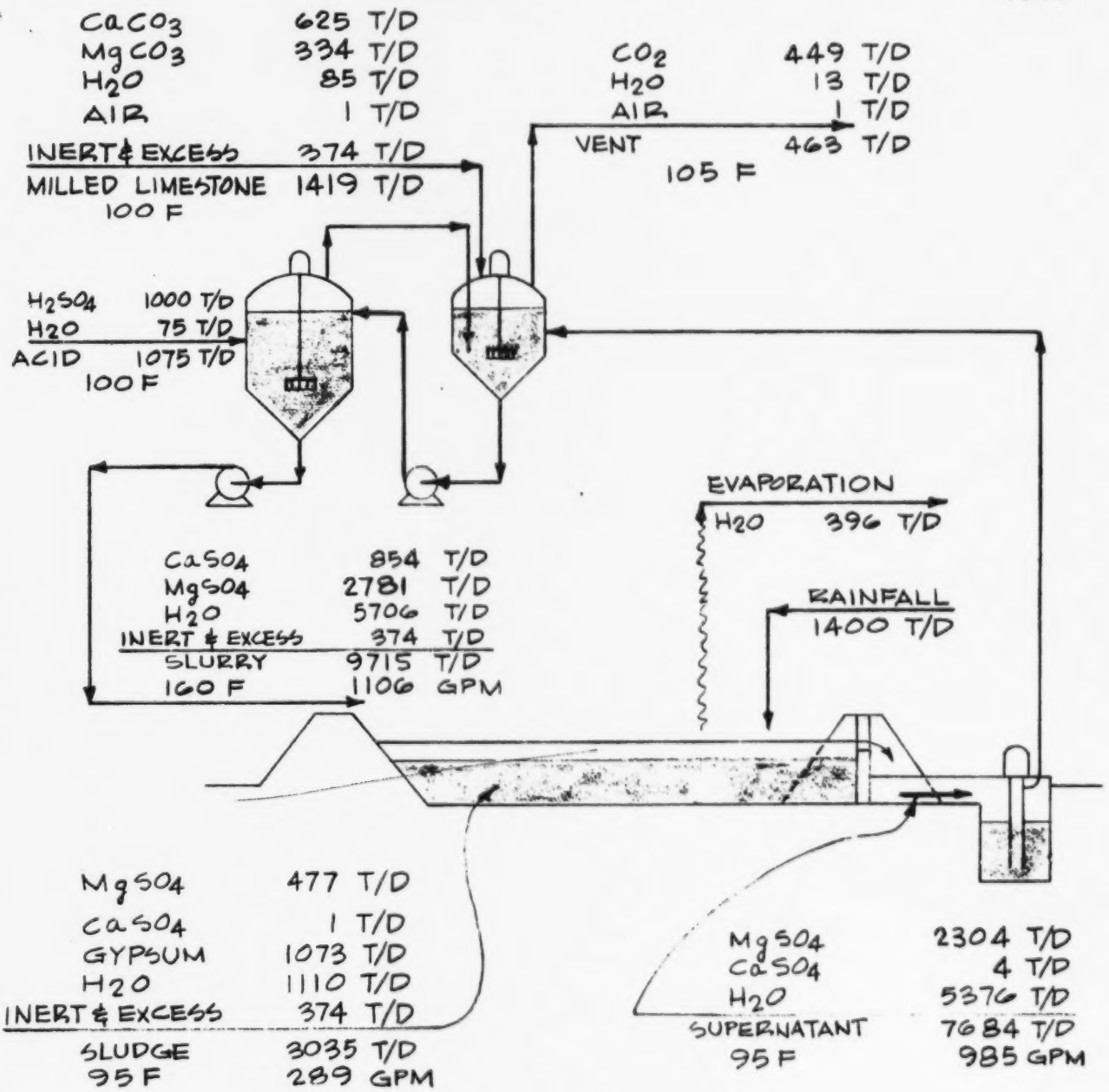
APPENDIX A - PROCESS FLOW DIAGRAM

PR 109

Job EPA | PROCESSES RESEARCH, INC. | File No 03389 Sheet No A-1

Location USA | INDUSTRIAL PLANNING AND RESEARCH | Checked by ____ Date ____

Subject H_2SO_4 NEUTRALIZATION | CINCINNATI NEW YORK | Computed by WDB Date APRIL 1973



H_2SO_4 LIMESTONE SLURRY NEUTRALIZATION PROCESS

APPENDIX B - PROCESS ECONOMICS

ECONOMICS OF LIMESTONE NEUTRALIZATION

FOR 100 TONS H_2SO_4 DAILY

Investment	
Grinding and Neutralization	$600,000
Land for Ten Annual Ponds, $500 per Acre	15,000
Annual Gypsum Disposal Pond	160,000
Total Investment	$775,000

Daily Operating Cost	All Acid Neutralized	No Acid Neutralized
Interest, Taxes, and Insurance, Annually 7 percent of Investment	$ 155	$ 155
Depreciation, Grinding and Neutralization, Annually 10 percent of Investment	172	172
Depreciation, Annual Pond	457	46
Maintenance, with Overhead, Annually 5 percent of Investment	111	111
Labor, with Overhead, $7 per Hour	336	-
Power, 1.5 cents per Kwh	72	-
Limestone, delivered, $3 per Ton	426	-
Total Daily Operating Cost	$1,729	$ 484
Incremental Operating Cost per Ton H_2SO_4	$17.29	$ 4.84
Incremental Abatement Cost per Ton Sulfur	$52.85	$14.80
Daily Sulfur Tonnage	33	33

ECONOMICS OF LIMESTONE NEUTRALIZATION

FOR 350 TONS H_2SO_4 DAILY

Investment	
Grinding and Neutralization	$1,160,000
Land for Ten Annual Ponds, $500 per Acre	45,000
Annual Gypsum Disposal Pond	325,000
Total Investment	$1,530,000

Daily Operating Cost	All Acid Neutralized	No Acid Neutralized
Interest, Taxes, and Insurance, Annually 7 percent of Investment	$ 306	$ 306
Depreciation, Grinding and Neutralization, Annually 10 percent of Investment	331	331
Depreciation, Annual Pond	928	93
Maintenance, with Overhead, Annually 5 percent of Investment	219	219
Labor, with Overhead, $7 per Hour	560	-
Power, 1.5 cents per Kwh	229	-
Limestone, delivered, $3 per Ton	1,494	-
Total Daily Operating Cost	$4,067	$ 949
Incremental Operating Cost per Ton H_2SO_4	$11.63	$ 2.71
Incremental Abatement Cost per Ton Sulfur	$35.60	$ 8.29
Daily Sulfur Tonnage	114	114

ECONOMICS OF LIMESTONE NEUTRALIZATION

FOR 1,000 TONS H_2SO_4 DAILY

Investment	
Grinding and Neutralization	$2,080,000
Land for Ten Annual Ponds, $500 per Acre	125,000
Annual Gypsum Disposal Pond	670,000
Total Investment	$2,875,000

Daily Operating Cost	All Acid Neutralized	No Acid Neutralized
Interest, Taxes, and Insurance, Annually 7 percent of Investment	$ 575	$ 575
Depreciation, Grinding and Neutralization Annually 10 percent of Investment	594	594
Depreciation, Annual Pond	1,915	192
Maintenance, with Overhead, Annually 5 percent of Investment	411	411
Labor, with Overhead, $7 per Hour	700	-
Power, 1.5 cents per Kwh	512	-
Limestone, delivered, $3 per Ton	4,254	-
Total Daily Operating Cost	$8,961	$1,772
Incremental Operating Cost per Ton H_2SO_4	$ 8.96	$ 1.77
Incremental Abatement Cost per Ton Sulfur	$27.40	$ 5.41
Daily Sulfur Tonnage	327	327

ECONOMICS OF LIMESTONE NEUTRALIZATION

FOR 350 TONS H_2SO_4 DAILY

Smelter Offgas Pollution Abatement Costs	2 Mole Percent SO_2 In Smelter Offgas	6 Mole Percent SO_2 In Smelter Offgas	12 Mole Percent SO_2 In Smelter Offgas
Acid Plant Operating Costs, per Ton Sulfur	$ 78	$ 33	$ 25
Neutralization Operating Costs, per Ton Suflur	36	36	36
Total Abatement Costs, per Ton Sulfur	$114	$ 69	$ 61
Daily Sulfur Tonnage	114	114	114

APPENDIX C - AMERICAN SMELTING AND REFINING COMPANY DATA

ASARCO

AMERICAN SMELTING AND REFINING COMPANY
CENTRAL RESEARCH LABORATORIES
SOUTH PLAINFIELD, N. J. 07080

WILLIAM P. ROE
DIRECTOR OF RESEARCH
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MANAGER, MINERALS RESEARCH
H. E. HOWE
MANAGER, METALS RESEARCH

March 13, 1972

Mr. Norman Plaks, Chief
Industrial Process Section
Demonstration Projects Branch
Control Systems Division
Environmental Protection Agency
Research Triangle Park, N. C. 27711

Dear Mr. Plaks:

Your letter of February 7 has been received and I wish to thank you for the brief report on neutralization of abatement derived sulfuric acid.

Our investigation of limerock neutralization has been strictly of a laboratory nature with the emphasis directed primarily at determination of limerock requirements and the extent to which calcium and magnesium are solubilized. Two different limerocks, having the following analyses, have been employed in this study.

Limerock No. 1		Limerock No. 2	
CaO	47.3%	CaO	48.2%
MgO	0.9	MgO	3.3
FeO	0.4	FeO	0.4
SiO_2	1.0	SiO_2	4.5

Two methods of effecting neutralization have been examined. The first of these, which in terms of possible future scale-up, may be considered similar to the first step of the wet process for producing phosphoric acid, involved addition of ground limerock, slowly with continuous stirring, to a dilute sulfuric acid solution (100 gm H_2SO_4/liter). Following addition of the limerock stirring was continued for 30 minutes and then the pH of the resultant slurry was determined. From a number of such tests involving differing limerock additions, a series of curves were developed depicting slurry pH, at the end of an essentially constant reaction time, expressed as a function of limerock addition.

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The second method of neutralization, in terms of possible future large scale application, may be considered similar to the den method for producing superphosphate. Here a fixed volume of concentrated sulfuric acid was slowly added to a known weight of ground limerock. The acid-limerock mixture was prepared in a mortar and lightly "worked" with a pestle as the acid was added. Following mixing of acid and limerock, which required five to ten minutes, the essentially dry product was allowed to stand for an hour, was sampled, and then leached with water. Measurement of the pH of the leach solution gave an indication of the extent to which neutralization was effected in the allocated reaction time. Leach solutions were also analyzed to determine soluble calcium and magnesium.

For purposes of the discussion to follow, the two methods of neutralization hereafter will be referred to simply as the wet method and the dry method respectively. Fineness of grind of the limerock was another variable examined in this laboratory investigation. Following is a tabulation of screen analyses of limerock used in the neutralization study:

Limerock No. 1				Limerock No. 2			
Grind No. 1		Grind No. 2		Grind No. 1		Grind No. 2	
+60 mesh	32.0%	+100 mesh	1.0%	+60 mesh	7.0%	+100 mesh	2.0%
-60+100	18.0	-100+200	3.9	-60+100	7.6	-100+200	7.0
-100+200	11.0	-200+325	9.0	-100+200	24.3	-200+325	11.0
-200	39.0	-325	87.0	-200+325	15.4	-325	80.0
				-325	45.7		

"Wet Process" Neutralization

Typical curves, depicting slurry pH as a function of limerock addition, are illustrated in Figure No. 1. It is essential to recognize that these curves do not depict the addition of an increasing weight of limerock to a single sample of sulfuric acid. Rather, to illustrate the effect of the degree of grinding, each of the plotted points represents a test in which the indicated weight of limerock was added to 300 ml of dilute sulfuric acid (100 gm H_2SO_4/liter) and allowed to react for a period of 30 minutes. For example, from the curves of Figure No. 1

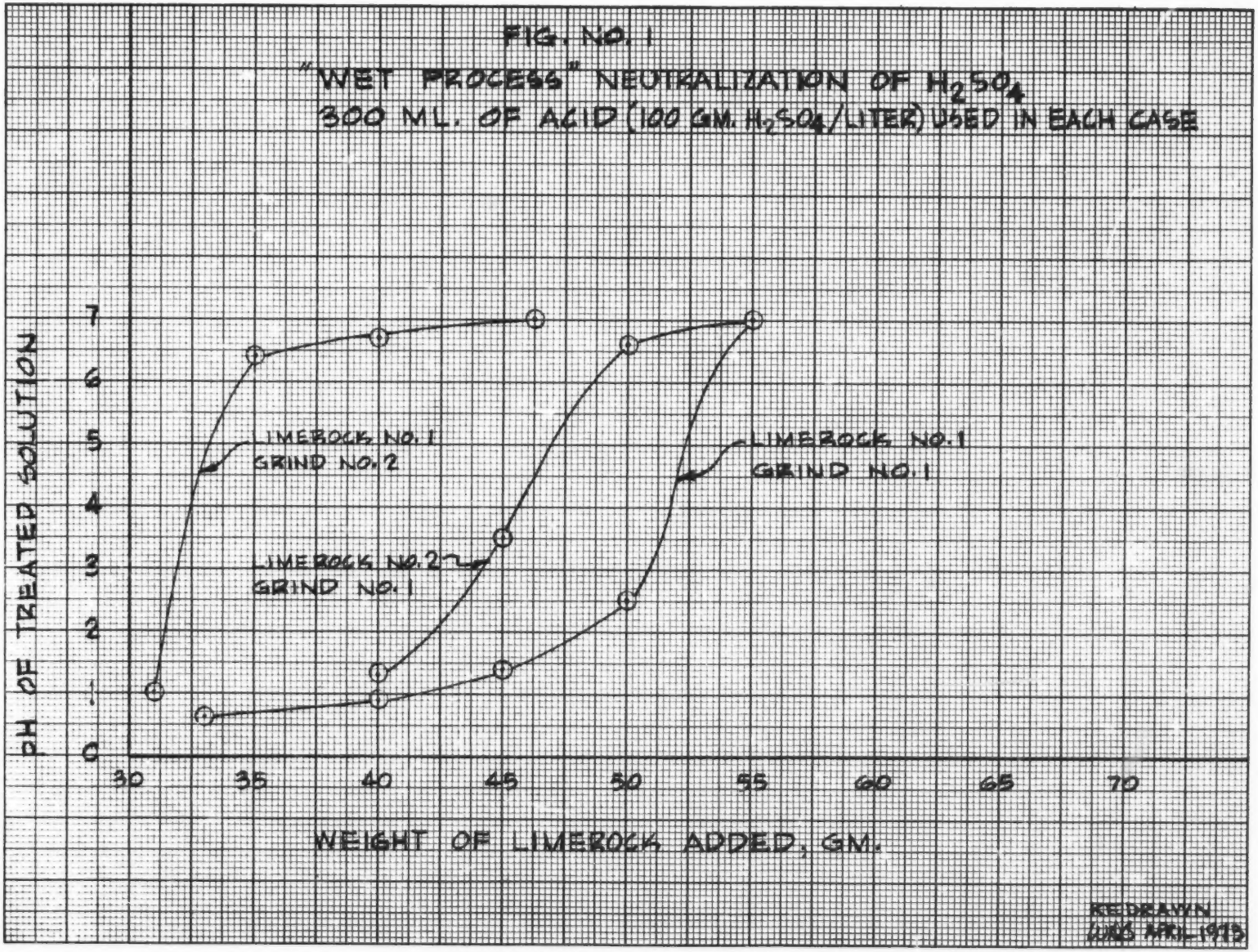


FIG. NO. 1
"WET PROCESS" NEUTRALIZATION OF H_2SO_4
300 ML. OF ACID (100 GM. H_2SO_4/LITER) USED IN EACH CASE
pH OF TREATED SOLUTION
0
1
2
3
4
5
6
7
30
35
40
45
50
55
60
65
70
WEIGHT OF LIMEROCK ADDED, GM.
LIMEROCK NO. 1
GRIND NO. 2
LIMEROCK NO. 2
GRIND NO. 1
LIMEROCK NO. 1
GRIND NO. 1
KEDRAVN
JUNE APRIL 1915

it may be estimated that 38 gms of the very finely ground limerock would be required to reach a slurry pH of 6.5 while 54 gms of the relatively coarsely ground limerock would be required to attain this same pH. These weights correspond respectively to approximately 107% and 151% of stoichiometric. With an intermediate grind, i.e. Limerock No. 2, Grind No. 1, approximately 144% of stoichiometric would be required to attain a slurry pH of 6.5.

Thus, it is evident that fineness of grind could be extremely important insofar as actual limerock requirement for acid neutralization is concerned. With increasing reaction time differences in limestone requirement attributable to varying fineness of grind tend to decrease. For example, with a 6.5 hour reaction time rather than the 0.5 hour reaction time depicted in Figure No. 1, the neutralization efficiency of Grind No. 1 for Limerock No. 1 was essentially the same as that of Grind No. 2 for Limerock No. 1 at the much shorter reaction time. This is, of course, consistent with the frequently cited observation that precipitation of calcium sulfate tends to "blind" the surface of, at least, the coarser particles of limerock.

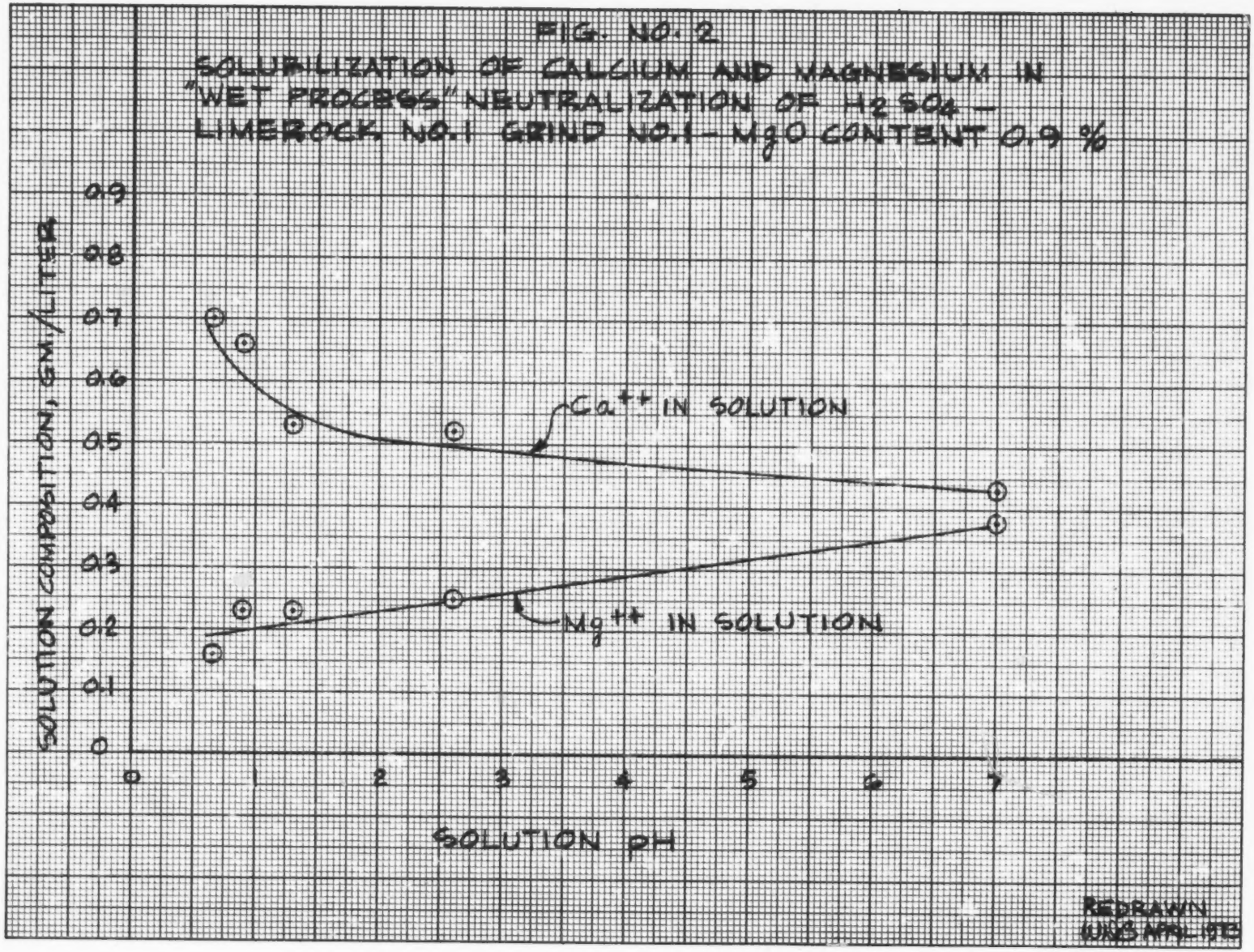
At this point in time we have not attempted to determine the optimum degree of grind. Discounting, for the moment, the importance of such factors as magnesium solubilization, optimum grind would, of course, be dependent upon such cost related determinants as power cost for grinding versus power cost for agitation, capital cost for grinding equipment versus capital cost of reaction vessels, etc. It would appear, however, that any attempt to determine optimum degree of grind should be based on data derived by using somewhat larger scale equipment, i.e. a small pilot plant, in order to obviate uncertainties associated with direct scale-up from beaker tests.

Solubilization of calcium and magnesium is illustrated in Figures No. 2 and 3 where concentrations of calcium and magnesium are plotted as a function of solution pH. As in Figure No. 1, each point on these curves represents the addition of differing amounts of limerock to a fixed volume of dilute (100 gm H_2SO_4/liter) acid solution with reaction time being a constant 30 minutes. At this time we are unable to account for the differing behavior of magnesium in the two series of tests, i.e. generally increasing dissolution of magnesium as solution pH increases over the range of approximately 1 to 7 in the case of the limerock of lower MgO content and generally constant dissolution of magnesium with increase in solution pH from approximately 1 to 7 for the limerock of higher MgO content.

Referring to Figure No. 3 it will be noted that in one test solution pH was increased to a value of 9.5. This was effected by the addition of hydrated lime after the acid had been essentially neutralized by limerock. As would be expected, magnesium solubility was somewhat decreased at this higher pH.

FIG. NO. 2

SOLUBILIZATION OF CALCIUM AND MAGNESIUM IN "WET PROCESS" NEUTRALIZATION OF H_2SO_4 – LIMEROCK NO.1 GRIND NO.1 – MgO CONTENT 0.9 %



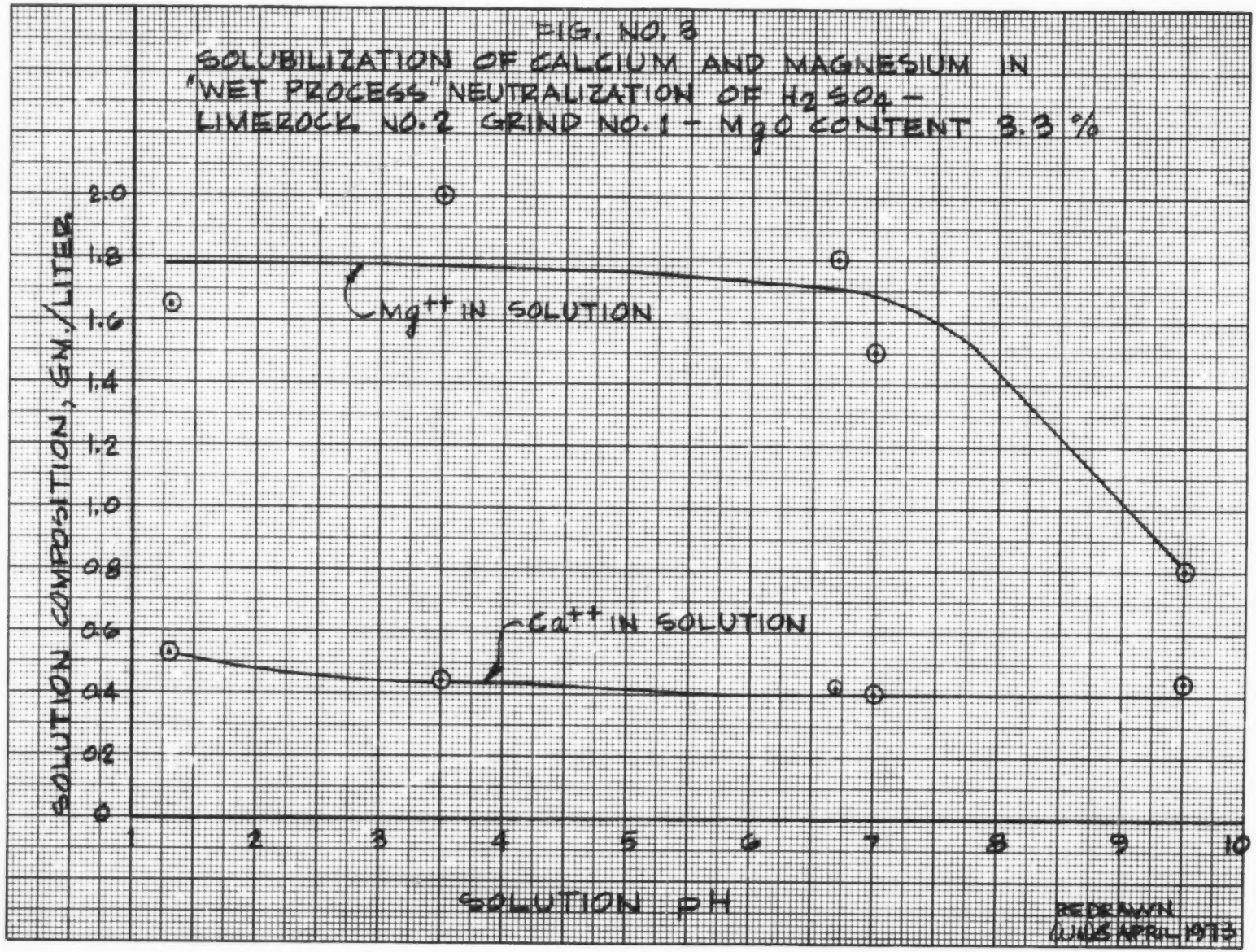


FIG. NO. 3
SOLUBILIZATION OF CALCIUM AND MAGNESIUM IN "WET PROCESS" NEUTRALIZATION OF H_2SO_4 – LIMEROCK NO. 2 GRIND NO. 1 – MgO CONTENT 3.3 %
SOLUTION COMPOSITION, GM./LITER
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
Mg^{++} IN SOLUTION
Ca^{++} IN SOLUTION
1
2
3
4
5
6
7
8
9
10
SOLUTION pH
REDRAWN 4/1975

In a practical sense it is perhaps more meaningful to compare the percentages of total magnesium solubilized with the acid essentially neutralized, i.e. at a solution pH of 6.5-7.0. With the limerock more finely ground, 33-34% of the total magnesium was solubilized with final solution pH at 6.5-7.0 regardless of whether the acid was neutralized with the limerock of higher (3.3%) MgO content or the limerock of lower (0.9%) MgO content. In neutralizing acid with the very finely ground limestone of the higher MgO content and subsequently increasing slurry pH to 9.5 through the addition of hydrated lime, 20% of the total magnesium remained in solution.

The degree of grind of the limerock also has a rather pronounced effect on magnesium solubilization. For example, in neutralizing acid with limerock of the lower MgO content (reaction time being constant at 30 minutes) 33% of total magnesium in the limerock appeared in the final neutral solution. However, since the actual limerock requirement for neutralization amounted to 107% of stoichiometric for the more finely ground material and 151% of stoichiometric for the more coarsely ground material, absolute solubilization of magnesium was 41% greater in the case of the latter.

"Dry Process" Neutralization

In the "dry process" neutralization tests limerocks, again differing with respect to both composition and grind, were employed. After thorough mixing of limerock and acid, each cake was allowed to stand for one hour and was then leached in water. The soluble magnesium contents, as well as the pH, of the resultant solutions were determined. Solution pH is plotted in Figure No. 4 as a function of the weight of limerock added to individual samples of acid and again, as in "wet neutralization," the efficiency with which the limerock is utilized is shown to be highly dependent upon fineness of grind. From the curves it may be estimated that limerock requirements to effect neutralization, i.e. to attain a pH of 6.5, for the four limerock samples are as follows:

Limerock	Grind	Limerock Requirement, % of Stoichiometric
No. 1	No. 2 87.0%-325 mesh	103
No. 2	No. 2 80.0%-325 "	122
No. 2	No. 1 45.7%-325 "	160
No. 1	No. 1 39.0%-200 "	197

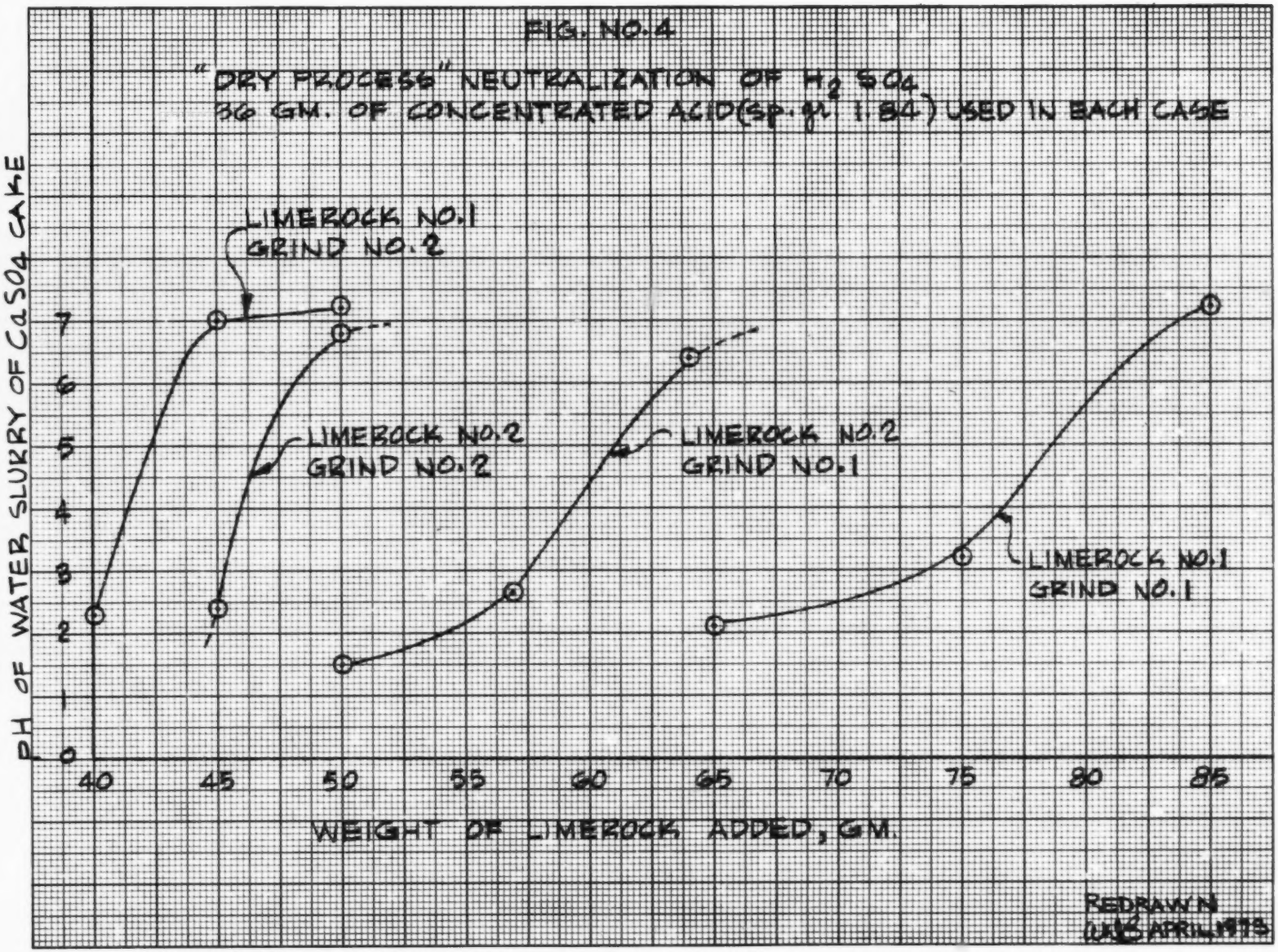


FIG. NO. 4
"DRY PROCESS" NEUTRALIZATION OF H_2SO_4
36 GM. OF CONCENTRATED ACID (Sp. gr. 1.84) USED IN EACH CASE
LIMEROCK NO.1
GRIND NO.2
LIMEROCK NO.2
GRIND NO.2
LIMEROCK NO.2
GRIND NO.1
LIMEROCK NO.1
GRIND NO.1
PH OF WATER SLURRY OF $CaSO_4$ CAKE
0
1
2
3
4
5
6
7
40
45
50
55
60
65
70
75
80
85
WEIGHT OF LIMEROCK ADDED, GM.
REDRAWN

Generally speaking, a higher percentage of the magnesium content of the limerock was rendered water soluble in "dry process" neutralization as compared to "wet process" neutralization. The extent of magnesium solubilization for the "dry process" tests are tabulated as follows:

Limerock	Grind	Magnesium Solubilization, % of Total Magnesium
No. 1	No. 1 39.0%-200 mesh	41
No. 1	No. 2 87.0%-325 "	68
No. 2	No. 1 45.7%-325 "	72
No. 2	No. 2 80.0%-325 "	77

As in those tests involving "wet process" neutralization, a greater percentage of total magnesium in the limerock was solubilized as fineness of grind increased. However, for both the limerock of low magnesium content and the limerock of higher magnesium content, absolute magnesium solubilization decreased with increasing fineness of grind due to the fact that a lesser weight of limerock was required to neutralize the acid in the case of the more finely ground material.

General

Insofar as the feasibility of limerock neutralization of abatement acid is concerned, we share the concern of others in regard to potential hazards involved in storage of vast quantities of waste material containing quite significant tonnages of soluble magnesium sulfate. Consider for the moment, neutralization of 1000 tons of sulfuric acid/day with limerock having a composition equivalent to that previously denoted Limerock No. 1, i.e. 0.9% MgO. Here there is the potential to produce (depending, of course, upon the extent to which the magnesium were solubilized) as much as 48.1 tons of soluble Epsom salts/day, equivalent on a yearly basis to approximately 17,600 tons. Even if only 20-30% of the magnesium were converted to the sulfate this would be, in my opinion, a tremendous amount of soluble material to put out on a dump subject to rainfall. I am, of course, well aware that your organization, as well as other interested groups, recognize this problem and that considerable attention has been and continues to be given to its solution.

We are pleased to be able to contribute the data herein, limited though it is in comparison to the total required before large scale neutralization of abatement derived sulfuric acid can be effected with at least

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an approach to optimization of the several controlling parameters and some assurance of the safety of disposing of the waste material. We would appreciate having a copy of the current study when it is completed.

Very truly yours,

James M. Henderson

JMH/hb

March 31, 1972

Mr. C. S. Haselberger
Environmental Protection Agency
Office of Air Programs
Research Triangle Park
North Carolina 27711

Subject: Neutralization of Abatement Derived
Sulfuric Acid
Task No. 3, Contract No. 68-02-0242
ASARCO Data

Dear Mr. Haselberger:

Reference is made to American Smelting and Refining Company letter dated March 13, 1972, a copy of which was enclosed with your letter to us dated March 24, 1972. In our review of the data, some questions have arisen which you may wish to discuss with ASARCO.

In Figure No. 1, regarding the "wet process," a data point appears at 33 grams and pH 0.65 without indication to which limerock this point refers, except coincidence of pH of data points in Figure No. 2. It would be helpful to have confirmation by ASARCO that the 33 grams pH 0.65 data point in Figure No. 1 is for Limerock No. 1 Grind No. 1.

Also with regard to Figure No. 1, it would be helpful to have information from ASARCO on the grams of Limerock No. 1 Grind No. 1 added for pH 4.5.

In Figure No. 2 and Figure No. 3, regarding the solubilization of calcium and magnesium in the "wet process," the limerock grinds and the amounts of limerock and acid are not indicated except by coincidence of pH of data points in Figure No. 1. It would be helpful to have confirmation by ASARCO that Figure No. 2 refers to Limerock No. 1 Grind No. 1 and that Figure No. 3 refers to Limerock No. 2 Grind No. 1.

The comments in the first paragraph on page 4 appear to refer, not to Figure No. 2 nor Figure No. 3, but to tests run on limerock "more finely ground" than Limerock No. 1 Grind No. 1 and Limerock No. 2 Grind No. 1. It would be helpful to have confirmation by ASARCO that the first paragraph on page 4 refers to Limerock No. 1 Grind No. 2 and Limerock No. 2 Grind No. 2.

Also regarding Limerock No. 2 Grind No. 2, it would be helpful to have information from ASARCO on the grams of limerock added to 300 ml of acid for pH 6.5 to 7.0 at 30 minutes.

In Figure No. 4, regarding the "dry process," the left most set of data points appear incorrectly designated Limerock No. 1 Grind No. 1. It would be helpful to have confirmation by ASARCO that the left most set of data points in Figure No. 4 actually refer to Limerock No. 1 Grind No. 2.

Also with regard to Figure No. 4, we presume that about 280 ml of water was used in leaching each cake. It would be helpful to have confirmation of this by ASARCO, as this bears on the significance of the pH observed.

Referring to the percentages of magnesium solubilization for the "dry process" tabulated in the first paragraph on page 5, we presume that these data refer to pH 6.5 solutions. It would be helpful to have confirmation of this by ASARCO.

Very truly yours,

PROCESSES RESEARCH, INC.

W. D. Beere
Project Manager

WDB/pm

cc: M. R. Jester
P. W. Speite

April 4, 1972

Mr. G. S. Haselberger
Environmental Protection Agency
Office of Air Programs
Research Triangle Park
North Carolina 27711

Subject: Neutralization of Abatement Derived
Sulfuric Acid
Tank No. 3, Contract No. 68-02-0242
ASARCO Data

Dear Mr. Haselberger:

An additional question has arisen in our review of the American Smelting and Refining Company letter dated March 13, 1972.

In Figure No. 4 regarding the "dry process," 36 grams concentrated acid is said to have been used for each cake. We had presumed that this was 30 grams H_2SO_4 and 6 grams water, there having been 30 grams H_2SO_4 used in each "wet process" case. Six grams water would be the least adequate for the production of gypsum ($CaSO_4 \cdot 2H_2O$) by reacting 30 grams H_2SO_4 with $CaCO_3$.

The specific gravity of acid containing 30 grams H_2SO_4 and 6 grams water would be about 1.77, this being 83.3 percent H_2SO_4. This is not consistent with the indication in Figure No. 4 that the concentrated acid had specific gravity 1.84.

Thirty-six grams of acid having specific gravity 1.84 would contain more than 34 grams H_2SO_4 and less than 2 grams water, this being insufficient water for production of gypsum by reacting 34 grams H_2SO_4 with $CaCO_3$.

It would be helpful to have information from ASARCO regarding the proportions of H_2SO_4 and water in the 36 grams concentrated acid used for each cake in the "dry process."

Very truly yours,

PROCESSES RESEARCH, INC.

W. D. Beers
Project Manager

WDB/pm

cc: M. R. Jester
P. W. Spaite

ASARCO

AMERICAN SMELTING AND REFINING COMPANY
CENTRAL RESEARCH LABORATORIES
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WILLIAM P. ROE
DIRECTOR OF RESEARCH
VAL KUDRYK
MANAGER, MINERALS RESEARCH
H. B. HOWE
MANAGER, METALS RESEARCH

April 11, 1972

Mr. G. S. Haselberger
Environmental Protection Agency
Industrial Process Section
Demonstration Projects Branch
Control Systems Division
Research Triangle Park, North Carolina 27711

Dear Mr. Haselberger:

This is in reply to your letter of April 6, your handwritten memorandum of the same date and the attachments dated March 31 and April 4 respectively in which Mr. W. D. Beers, Project Manager for Process Research, Inc. raises a number of questions relative to data included in my letter of March 13 to your Mr. Norman Plaks. Answers to the several questions of Mr. Beers follow:

A. With reference to Mr. Beers letter of March 31, 1972-

(1) As surmised by Mr. Beers, the data point appearing in Figure No. 1 attached to my letter of March 13, corresponding to a pH of 0.65 and a limerock addition of 33 grams is, in fact, for Limerock No. 1, Grind No. 1. I should have extended the curve for this particular limerock to the lower pH value.

(2) All available data points are indicated in Figure No. 1. At this time, the grams of Limerock No. 1, Grind No. 1 required to yield a solution pH of 4.5 can only be estimated by interpolation.

(3) Figure No. 2 does represent data pertaining to use of Limerock No. 1, Grind No. 1. The two data points corresponding to a solution pH of 4.5 represent a reaction time of 50 minutes rather than 30 minutes and, therefore, were incorrectly included in this plot. Figure No. 3 does represent Limerock No. 2, Grind No. 1.

(4) Comments made in the first paragraph on page 4 of my letter of March 13 do refer to Figures No. 2 and 3 as would be implied by the two preceding paragraphs. In referring to the "more finely ground" limerock I merely meant the more finely ground of the two limerocks used in the series of tests depicted in Figures No. 2 and 3, i.e. Limerock No. 2, Grind No. 1.

(5) I regret any chance implication that each of the four limerock samples was used in both "wet and dry process" neutralization tests for this is not the case. Only three limerock samples were employed in the "wet process" tests, as indicated in Figure No. 1.

(6) Mr. Beers is correct in that the left most set of data points in Figure No. 4 should have beeh designated Limerock No. 1, Grind No. 2.

(7) As will be noted in Figure No. 4 of my letter of March 13, the amount of limerock actually used in each of the several "dry process" neutralization tests illustrated varied considerably. Similarly, the amount of water used in leaching of the cakes was varied so as to maintain an approximately equivalent liquid to solids ratio. Actual water used in the leaches ranged from 330 ml to 650 ml.

(8) The comments in the first paragraph of page 5 relative to magnesium solubilization do refer only to those dry process neutralization tests in which sufficient limerock was added to neutralize the acid , yielding leach solutions having a pH of 6.5 to 7.2, i.e. corresponding to the uppermost point on each of the curves of Figure No. 4.

B. With reference to Mr. Beers letter of April 4 -

(1) As indicated, 36 grams of concentrated sulfuric acid (sp. gr. of 1.84) was used in each of the "dry process" tests. I will concede that this acid provides insufficient water to form $CaSO_4 \cdot 2H_2O$.

Very truly yours,

James M. Henderson

JMH/hb

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